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Reactions of Technetium Hexafluoride with Nitric Acid, Nitrosyl Fluoride, and Nitryl Fluoride

The problem:

To determine the reactions of technetium hexafluoride with nitric oxide, nitrosyl fluoride, and nitryl fluoride. The reactions of various hexafluorides with nitrogen oxides and nitrogen oxide fluorides have recently been studied increasingly. In particular, the reactions of third-transition-series hexafluorides with nitric oxide and nitrosyl fluoride have been used for assessment of the relative oxidizing powers of these hexafluorides. Of the thermodynamically stable metal hexafluorides, least is known about technetium hexafluoride, possibly because the radioactivity of technetium has inhibited experimental work.

The solution:

Reactions of technetium hexafluoride with nitric oxide, nitrosyl fluoride, and nitryl fluoride gave the compounds NOTcF_6 , $(\text{NO})_2\text{TcF}_8$, and NO_2TcF_7 . The stoichiometry of each reaction was studied. The magnetic properties and infrared spectra of these compounds were studied and compared with those of some analogous complexes of the hexafluorides of tungsten, rhenium, and osmium. Attempts to prepare NOTcF_7 were unsuccessful.

How it's done:

A vacuum manifold of monel and nickel was used for all experimental manipulations. Reactions were carried out either in thin-walled (1/32 in.) nickel weighing cans, fitted with small brass valves, or in 3/4-in. Kel-F test tubes fitted with Kel-F valves. The metal vacuum system and reaction vessels were passivated with fluorine and chlorine trifluoride prior to use. Stoichiometries of the reactions were followed

by weighing both starting materials and reaction products in tared reaction vessels.

Considerable difficulties were encountered in chemical analyses of the samples. In general, fluoride analyses were low owing to the exceptional stability of the TcF_6^{-2} ion which is formed upon hydrolysis of the solids. Technetium analyses were performed by evaporation of aliquots of the solutions on platinum plates, and counting of the Tc^{99} betas in a calibrated PCC-10 proportional counter having an overall geometry factor of 0.785. These results are somewhat uncertain because of self-absorption of the soft betas in the solid sample. However, the reproducibilities of reaction stoichiometries, combined with supporting evidence of physical properties, leave little doubt as to the correctness of the stated compositions.

The infrared, x-ray-diffraction, and magnetic-susceptibility samples were prepared in a small, nitrogen-filled, dry box under slight positive pressure. The details of and methods for the specific reactions with technetium hexafluoride are available.

Notes:

1. This information may interest physical chemists doing transition-metal research.
2. Inquiries concerning this information may be directed to:

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Patent status:

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